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Studies of the hydrogen bond. III

Molecular orbital treatment of some saturated and unsaturated ethers

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Introduction

The concept of the hydrogen bond is generally accepted among chemists, although the precise nature of hydrogen bonding is still not fully understood. Some experimental evidence on the hydrogen bond, and viewpoints as to its character were reported in two preceeding papers of this series (EHRENBERG and FISCHER [1]), in which the influence of adjacent double bonds on the ability of a "heteroatom" (N, O) to be "acceptor" in hydrogen bond formation was studied. In particular, the unsaturated compound divinyl ether, and the corresponding saturated compound, diethyl ether, were compared in respect of their admixture with water. Several experimental facts suggest that diethyl ether forms hydrogen bonds relatively easily, whereas divinyl ether has no tendency to enter into hydrogen bond formation.

In this paper some results of theoretical calculations of hyperconjugation energies, charge distributions, and bond-orders in these ether molecules are given, and some conclusions regarding hydrogen bonding by ethers are reached. The calculations were made using the molecular orbital (m. o) method (for a rewiew of this method: see COULSON [2]).

Method

The usual approximation made in applying the m. o. method to a conjugated system is to consider *only* the interactions of the π-electrons, and to neglect the σ-electrons entirely. We have followed this convention in the calculations of this paper. For a molecule of ν atoms, $\lambda, \mu \ldots$, and n π-electrons the j:th m. o., expressed in the LCAO (linear combination of atomic orbitals) approximation, is

$$\psi_j = \sum_{\mu} x_{j\mu} \varphi_{\mu}$$

where φ_{μ} is a normalised, hydrogenlike $2p$ orbital of the atom μ, and $x_{j\mu}$ is a parameter to be determined by a variational method. The normalisation condition of the m. o. is

$$\int \psi_j^* \psi_j \, d\tau = \sum_{\lambda, \mu} x_{j\lambda} x_{j\mu} S_{\lambda\mu} = 1,$$

where $S_{\lambda\mu} = \int \varphi_\lambda^* \varphi_\mu \, d\tau$ is the overlap integral. The energy of the electron, E_j, is

$$E_j = \int \psi_j^* H \psi_j \, d\tau$$

where H is the one-electron Hamiltonian appropriate to a self-consistent field. The variational treatment gives in the usual way the determinantal equation

$$|H_{\lambda\mu} - E S_{\lambda\mu}| = 0 \tag{1}$$

where $H_{\lambda\mu} = \int \varphi_\lambda^* H \varphi_\mu \, d\tau$. $H_{\lambda\lambda} = \alpha_\lambda$ is a Coulomb integral and $H_{\lambda\mu} = \beta_{\lambda\mu}$ an exchange integral. Equ. (1) is of the ν:th degree in E. To each root, E_j, corresponds a set of parameters, $x_{j\mu}$, which determine the j:th m. o. In the ground level two electrons occupy each of the m. o:s corresponding to the lowest energy values.

When overlap is included the electron charge on the atom λ, q_λ, and the π-bond order between the atoms λ and μ, $p_{\lambda\mu}$, are defined by Coulson (private communication) as:

$$q_\lambda = \sum_j x_{j\lambda} y_{j\lambda} \qquad (j = \text{occupied m. o:s})$$

$$p_{\lambda\mu} = \tfrac{1}{2} \sum_j (x_{j\lambda} y_{j\mu} + x_{j\mu} y_{j\lambda})$$

where

$$y_{j\mu} = \sum_\lambda S_{\lambda\mu} x_{j\lambda}.$$

Now it is convenient (see *e. g.* WHELAND [3] and MULLIKEN *et al.* [4]) to introduce a quantity γ:

$$\gamma_{\lambda\mu} = \beta_{\lambda\mu} - \tfrac{1}{2} S_{\lambda\mu} (\alpha_\lambda + \alpha_\mu) \tag{2}$$

γ is connected in a simple way with the bond energy, as shown below. Let

$$\alpha_c - E = z; \qquad \alpha_\mu - \alpha_c = 2\,\delta_\mu, \tag{3}$$

where δ_μ is a measure of the difference in electronegativity between the atom μ and the carbon atom. Introducing (2) and (3) in equ. (1), gives:

$$\begin{vmatrix} z + 2\,\delta_\lambda & \gamma_{\lambda\mu} + S_{\lambda\mu}(z + \delta_\lambda + \delta_\mu) \cdots\cdots \\ \gamma_{\lambda\mu} + S_{\lambda\mu}(z + \delta_\lambda + \delta_\mu) & z + 2\,\delta_\mu \qquad \cdots\cdots \\ \cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots \end{vmatrix} = 0. \tag{4}$$

Equ. (4) may be solved if we know the numerical values of γ and δ. Neither of these quantities are known exactly, but we can obtain probable values of γ and δ from their connexion with experimentally known bond energies, letting δ attain values reasonably compatible with the different proposed electronegativity scales (see *e. g.* PAULING [5], MULLIKEN [6]). This connexion is found by considering a m.o. extended over two atoms only, one of which is carbon. The highest root of (4) is:

$$z = -\delta_\mu + \frac{1}{(1-S_\mu^2)}\left[\gamma_\mu S_\mu - \sqrt{\delta_\mu^2(1-S_\mu^2)+\gamma_\mu^2}\right]$$

where the index C is omitted. If we assume that α_c and α_u have the same values for bonding and non-bonding electrons, the binding energy, D', is given by the expression:

$$D' = \alpha_c + \alpha_\mu - 2(\alpha_c - z) = \frac{2}{(1-S_\mu^2)}\left[\gamma_\mu S_\mu - \sqrt{\delta_\mu^2(1-S_\mu^2)+\gamma_\mu^2}\right] \qquad (5)$$

D' is approximately equal to the energy difference between a double and a single bond between the atoms in question, provided that all the quantities are referred to the same interatomic distance (for a detailed discussion on this point, see ROBERTS and SKINNER [7]). This is obtained through the construction of the Morse curves $D = D_0(1 - e^{-a(r-r_0)})^2$ of the bonds in question. D_0 is the dissociation energy, and the constant a is calculated from $a = \sqrt{k/2D_0}$, where k is the force constant. The values of these parameters used in the present paper are given in Table I.

Table I

Bond type	D_0 kcal	$r_0 \cdot 10^8$ cm	$k \cdot 10^{-5}$ dyn.cm^{-1}
C = C	145	1.33	9.9
C − C	83	1.54	3.8
C = O	156	1.21	12.0
C − O	80	1.43	4.4
C − H	98	1.09	4.9
O − H	110	0.96	8.2

The overlap integrals were evaluated using the $2p_z$ atomic wave functions given by DUNCANSON and COULSON [8]. The following screening constants were used: carbon 3.12, oxygen 4.70, hydrogen 1.16. As π-orbitals of the H_3- and H_2-groups we used the linear combination of atomic orbitals given by MULLIKEN *et al.* [4]. As to the values of δ and γ, we assigned reasonable values to δ and calculated the corresponding values of γ from equ. (5). In order to survey the influence of a variation in δ on charge distribution and bond order we performed the calculations with different sets of δ, γ-values. These are summarised in Table II. The values used for the CC-bonds are:

$$r_0 = 1.35\ \text{Å} \qquad S = 0.290 \qquad \gamma = 2.132\ \text{eV}$$

$$r_0 = 1.54\ » \qquad S = 0.213 \qquad \gamma = 1.147\ »$$

Table II

CO			CH		OH		
	$r = 1.43$ $S = 0.138$	$r = 1.42$ $S = 0.141$	$r = 1.09$ $S = 0.586$			$r = 1.0$ $S = 0.339$	$r = 1.6$ $S = 0.149$
$-2\,\delta_O$ eV	γ eV	γ eV	$+2\,\delta_H$ eV	γ eV	$-2\,\delta_{OH}$ eV	γ eV	γ eV
0.5	1.220	1.268	0.2	3.370	1.2	3.121	—
0.8	1.167	1.223	0.3	3.367	1.5	3.076	0.744
1.0	1.128	1.180	0.5	3.357	1.7	3.041	0.591
1.2	1.070	1.124	0.7	3.343			
1.5	0.956	1.013					

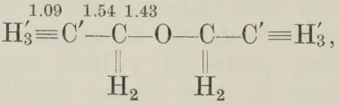
Results

Dimethyl ether. The structural formula of this molecule may be written $H_3\overset{1.09}{\equiv}C\overset{1.43}{—}O—C{\equiv}H_3$. We consider hyperconjugation involving two $2\,p_z$ electrons from the oxygen and one pair of π-electrons from each of the $H_3{\equiv}C$ triple bonds. In this as well as in the two following cases the secular equation may be factorised by considering the symmetry of the molecule, which permits a sub-division into orbitals symmetrical, ψ^s, and antisymmetrical, ψ^a, in the nuclei. The hyperconjugation energy, R, is given by:

$$R = 2\,(z_1^s + z_2^a + z_3^s) - 4\,z_2^a + 4\,\delta_O\,.$$

For this simple molecule the calculations were performed with several combinations of δ_H and δ_O values. Table III contains the computed values of hyperconjugation energy, charge distributions, and bond orders. We have tabulated the net charges, Q_μ, *i.e.* the sum of π-electronic and nuclear charges (the contribution from the σ-electrons is not taken into account). It is seen that for a given δ_O the charge on the oxygen atom and the bond order p_{CO} are almost unaffected by variations in δ_H. The hyperconjugation energy, however, varies considerably with both δ_O and δ_H. Furthermore, Table III shows that when $\delta_H \leq 0.3$ eV we obtain a larger, formal negative charge on H than on C. As this is rather improbable, we limit ourselves in the following to calculations with $\delta_H > 0.3$ eV.

Diethyl ether. This molecule, which has the formula



$$H_3'\overset{1.09}{\equiv}C'\overset{1.54}{—}\underset{\underset{H_2}{\|}}{C}\overset{1.43}{—}O—\underset{\underset{H_2}{\|}}{C}—C'{\equiv}H_3',$$

was treated analogously to dimethyl ether. The part of the hyperconjugation energy due to the inclusion of the oxygen atom, is given by the expression:

$$R = 2\sum_{j=1}^{5} z_j + 4\,\delta_O - 4\,(z_2^a + z_4^a).$$

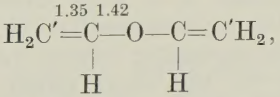
Table III

Dimethyl ether

$2\delta_H$ eV	Q_H	Q_c	Q_o	p_{HC}	p_{co}	R kcal
			$2\,\delta_o = -\,0.5$ eV			
0.2	−0.053	−0.022	+0.150	0.961	0.273	8.09
0.3	−0.039	−0.036	+0.148	0.962	0.270	7.72
0.5	−0.010	−0.062	+0.146	0.963	0.264	6.98
			$2\,\delta_o = -\,0.8$ eV			
0.2	−0.047	−0.020	+0.134	0.966	0.258	6.26
0.3	−0.032	−0.034	+0.132	0.966	0.255	5.91
0.5	−0.004	−0.061	+0.130	0.967	0.250	5.22
0.7	+0.024	−0.088	+0.128	0.967	0.244	4.53
			$2\,\delta_o = -\,1.0$ eV			
0.2	−0.042	−0.019	+0.122	0.969	0.246	4.92
0.3	−0.028	−0.033	+0.121	0.969	0.243	4.60
0.5	+0.001	−0.060	+0.118	0.970	0.238	3.95
0.7	+0.029	−0.088	+0.116	0.969	0.233	3.30
			$2\,\delta_o = -\,1.2$ eV			
0.2	−0.036	−0.019	+0.109	0.972	0.232	3.53
0.3	−0.022	−0.032	+0.108	0.972	0.230	3.23
0.5	+0.007	−0.060	+0.106	0.973	0.225	2.64
0.7	+0.035	−0.087	+0.104	0.973	0.220	2.03
			$2\,\delta_o = -\,1.5$ eV			
0.2	−0.026	−0.018	+0.087	0.978	0.208	1.41
0.3	−0.011	−0.032	+0.086	0.978	0.205	1.16
0.5	+0.017	−0.060	+0.084	0.978	0.201	0.65
0.7	+0.046	−0.088	+0.083	0.978	0.196	0.14

The numerical results obtained for diethyl ether are given in Table IV. For this molecule the values of the parameters δ_H and δ_o were varied within a smaller range than in the preceding case, partly because the calculations are much more cumbersome than those for dimethyl ether, partly because it was found, that the quantities, which are of special interest for the present investigation, *i.e.* Q_o, p_{co}, and R, are almost identical with the corresponding values of dimethyl ether.

Divinyl ether. For this molecule,



$$\mathrm{H_2C'}\overset{1.35}{=}\underset{\displaystyle \mathrm{H}}{\mathrm{C}}\overset{1.42}{-}\mathrm{O}-\underset{\displaystyle \mathrm{H}}{\mathrm{C}}=\mathrm{C'H_2},$$

the hyperconjugation energy is obtained from the expression:

$$R = 2 \sum_{j=1}^{3} z_j - 4 z_2^a + 4 \delta_O .$$

The computed values are summarised in Table V. Some computations were made with a 5 % lover value of S_{CO} in order to see how much this variation changes the results. The influence was found to be negligible.

Table IV

Diethyl ether

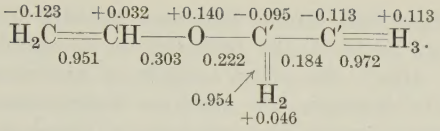
$Q_{H'}$	$Q_{C'}$	Q_H	Q_C	Q_O	$p_{H'C'}$	$p_{C'C}$	p_{HC}	p_{CO}	R kcal
		$2\delta_H = 0.5$ eV		$2\delta_O = -1.0$ eV					
+0.071	−0.070	−0.002	−0.057	+0.116	0.982	0.177	0.955	0.234	3.91
		$2\delta_H = 0.7$ eV		$2\delta_O = -1.0$ eV					
+0.100	−0.099	+0.026	−0.083	+0.113	0.980	0.183	0.953	0.228	3.28
		$2\delta_H = 0.5$ eV		$2\delta_O = -1.5$ eV					
+0.071	−0.071	+0.015	−0.056	+0.082	0.982	0.178	0.963	0.197	0.66
		$2\delta_H = 0.7$ eV		$2\delta_O = -1.5$ eV					
+0.100	−0.099	+0.042	−0.083	+0.080	0.979	0.184	0.961	0.192	0.17

Table V

Divinyl ether

$-2\delta_O$ eV	$Q_{C'}$	Q_C	Q_O	$p_{C'C}$	p_{CO}	R kcal
			$S_{CO} = 0.141$			
0.5	−0.181	+0.015	+0.332	0.906	0.415	14.76
0.8	−0.166	+0.022	+0.287	0.918	0.387	11.40
1.0	−0.153	+0.026	+0.255	0.927	0.366	9.08
1.2	−0.140	+0.029	+0.222	0.936	0.343	6.75
1.5	−0.117	+0.031	+0.171	0.951	0.303	3.32
			$S_{CO} = 0.135$			
0.5	−0.176	+0.015	+0.327	0.907	0.410	14.94
1.5	−0.113	+0.030	+0.168	0.952	0.299	3.59

Ethyl vinyl ether. We thought it of some interest to compute bond orders and charge distribution of the asymmetrical ethyl vinyl ether. The calculations were made with the following parameter values: $2\delta_O = -1.5$ eV, $2\delta_H = 0.5$ eV, $\alpha_C - \alpha_{C'} = 0.3$ eV; C belongs to the vinyl group and C′ to the ethyl group. The computed values of net charges and bond orders are indicated in the formula:



$$\overset{-0.123}{H_2C}\underset{0.951}{=\!=}\overset{+0.032}{CH}\underset{0.303}{—}\overset{+0.140}{O}\underset{0.222}{—}\underset{\underset{+0.046}{0.954\ H_2}}{\overset{-0.095}{C'}}\underset{0.184}{—}\overset{-0.113}{C'}\underset{0.972}{\equiv}\overset{+0.113}{H_3}.$$

It is seen that they agree well with the corresponding results for the symmetrical ethers.

Ether-water complexes. As is shown by COULSON and FISCHER [9] the simple m. o. method is unreliable when the interatomic distance is increased to more than $1.6\,r_0$. In most hydrogen-bonded molecular complexes the distance between the hydrogen of the one molecule and the oxygen of the other is near to this critical value. Though well aware of this fact we have made a tentative investigation of the hydrogen bond using the m. o. method in the crude form described above. Although one should not overemphasize the value of the results, it may be assumed that they give a correct qualitative description of the hydrogen bond.

We consider the system $>O' \underset{1.6}{\ldots\ldots} H \underset{1.0}{—} O\diagdown$, where O′ belongs to an ether. We assume that the three atoms lie on a straight line with the OH interatomic distances given in the formula. "Molecular" orbitals obtained from a combination of the atomic orbitals which have rotational symmetry around the nuclear axis lead to the charge distribution and bond orders collected in Table VI. It is seen from the Table that the σ-bond order between the hydrogen of the water and the oxygen of the ether, *i. e.* the bond order of the hydrogen bond, is around 0.2 for all the α_0- and $\alpha_{0'}$-values considered. A purely electrostatic interpretation of the hydrogen bond should require this bond order to be naught.

Table VI

Ether-water complex

$-2\,\delta_{HO'}$ eV	$-2\,\delta_{OH}$ eV	$Q_{O'}$	Q_H	Q_O	$p_{O'H}$	p_{HO}
1.5	1.5	+0.050	+0.232	−0.282	0.256	0.943
»	1.2	+0.041	+0.188	−0.229	0.247	0.954
1.7	1.7	+0.033	+0.267	−0.300	0.218	0.945
»	1.5	+0.032	+0.242	−0.273	0.211	0.952
»	1.2	+0.030	+0.191	−0.221	0.200	0.965

Discussion

Firstly, some conclusions may be drawn from the numerical results, with regard to the m. o. method. The value chosen for δ_μ affects to some extent the charge on the atom μ and the order of the bonds to this atom. The influence on other charges and bonds decreases rapidly with the distance. The influence from removed parts of the molecule is so small that a methyl group and an ethyl group affect the ether oxygen to the same extent (Tables III and IV). The similarity between the electron distribution of the asymmetrical ether and the symmetrical ones also emphasizes the fact, that removed parts of the molecule do not seriously influence one another. This result shows, that in the treatment of homologous molecules it is justified to use the same values of the parameters δ and γ. It also justifies the use of diatomic m. o:s in the calculation of corresponding δ- and γ-values (equ. (5)). The γ-values from (5) do not agree, however, with MULLIKEN's[1] suggestion that $\gamma/S =$ constant, which may depend on the approximations involved in both relations. The facts, well known from experiments, that bond energies and bond dipole moments are almost constant within a homologous series are in good agreement with the narrow range found for the influence of a variation of δ_μ. — The effect on bond order of a variation of δ and γ has earlier been discussed by COULSON [10], who varied δ and γ independently.

The value of the hyperconjugation energy is much more sensitive to a change in α than are charge and bond order. MULLIKEN [11] has shown that the α value of carbon varies from molecule to molecule, not only with a change from triple to double bond but also with the radicals bound to the atom. This emphasizes the extreme difficulty in choosing the "best" α value. When, as in the present case, the effects of hyperconjugation are studied it therefore seems better to draw conclusions from the calculations on bond order and charge distribution than from those of delocalisation energy.

The results obtained are subject to many uncertainties. We shall now discuss the influence of some of these factors. A questionable point is the expressions for the σ- and π-orbitals of the H_3- and H_2-groups. We have adopted the usual expressions though the overlap integral of the CH π-bond turns out to be twice as large as the overlap of the corresponding σ-bond. This result (also obtained by COULSON [12]) suggests that the π-bond should be stronger than the σ-bond, and needs further investigation. The point is, however, not of especial importance to the present results, as was shown by performing the computations with a 20 % lower value of D'_{CH}. This change in D' did not affect the net charge on the oxygen atom at all and only caused a small change in the charges on the carbon and hydrogen atoms. Nor are errors of a few percent in the assumed bond energies of importance.

The values of the overlap integrals depend on the screening constants, c, for the atomic wave functions, on the internuclear distances, r, and on the steric configuration of the molecules. It was found that the use of a c-value appropriate to O^+ instead of O (in the main computations we used a c-value between these) diminished the net charge by 4 %. The use of different screening constants for saturated and unsaturated ethers would not, therefore, diminish the ratio between their Q_0-values by more than 1 %. Even less is the effect of an error in r of the order 0.02 Å. The steric configuration of divinyl ether has been studied using the electron diffraction method by BASTIANSEN [13], to whom I am much indebted for performing that investigation. According to him, there seems to be a deviation from the planar configuration in divinyl ether, the C=C bonds making an angle of 15—20° with the plane of the C—O bonds. This will not, however, diminish the S-value by more than 5 %. This variation in S is considered in Table V.

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[1] Communicated on "Congrès de la liaison chimique", Paris 1948.

In the present investigation we have not accounted for orbital hybridisation. According to BASTIANSEN [13] the O—C—O angle is approximately the same in diethyl and divinyl ether. This means the same degree of hybridisation of the oxygen $2p$ orbitals occurs in the two compounds.

In general, the m. o. method will give comparable results in the case of similar molecules. This is certainly true in case of dimethyl ether and diethyl ether. As for divinyl ether there is reason to believe that this molecule is rather different from the saturated ethers. In our opinion, the main difference lies in a difference in the values of α_o and α_c and, consequently, of δ_o. From a study of the α_c-values computed by MULLIKEN [11] the conclusion can be drawn that the difference of $-2\delta_o$ between the saturated and unsaturated ethers most probably is less than 0.5 eV, divinyl ether having the higher value. In the computation for ethyl vinyl ether the difference was assumed to be 0.3 eV.

The values given in Tables III, IV, and V show clearly that the net charge and the bond order of the oxygen atom of saturated ethers are less than the corresponding quantities of unsaturated ethers. The hyperconjugation energy shows the same trend, though the result is less conclusive on this point. Analysing the influence of the various uncertainties considered above, we find that they will lower the ratio between the Q_o- and p_{co}-values of divinyl ether relatively to those of diethyl ether by less than 3 %. Consequently, we may draw the following conclusion: an adjacent double bond changes both the charge on an etheral oxygen atom and the C—O bond order, *i. e.* the polarisability of the oxygen atom.

In order to compare some of the theoretical values with experimental ones we choose as a probable case the one with $-2\delta_o$ of divinyl ether equal to 1.2 eV and the corresponding value of diethyl ether 1.0 eV. The tabulated Q_o-value of divinyl ether is $+0.22$ and that of diethyl ether $+0.11$. Because of the C—O σ-bonds the oxygen atom is negatively charged in both ethers though the computed π-electron distribution will diminish this charge, more in case of divinyl than of diethyl ether, the difference corresponding to a ~ 0.2 Debye smaller dipole moment. This agrees well with the experimental difference [1]: $1.23 - 1.06 = 0.17$ Debye. The computed p_{co}-values, 0.34 of divinyl and 0.23 of diethyl ether, means a bond length difference of 0.02 Å in good agreement with electron diffraction values.

We may now apply our results in respect of the nature of the hydrogen bond. The electrostatic energy of the complex considered above will be roughly proportional to $Q_{o'}$ as there is no reason to assume different O—O distances in the water complexes of the two ethers, which have almost the same sterical configuration around the oxygen atoms. Using the values of Q_o from Tables IV and V we find a difference in electrostatic energy between the complexes with water of diethyl and divinyl ether, which for all the $-2\delta_o$-values considered is less than 2 kcal/mole. This difference is less than half the energy of the hydrogen bond, which is known to vary between 4 and 8 kcal/mole. Thus, a purely electrostatic interpretation of the hydrogen bond is incomplete. We also have to consider polarisation effects. The formation of the hydrogen bond will disturb the hyperconjugation with the rest of the molecule of the $2p_z$ electrons of the ether oxygen. As p_{co} is 1.5 times as large in divinyl ether as in diethyl ether the activation energy for the water complex formation should be considerably larger in the case of divinyl ether. Thus, divinyl ether cannot enter into hydrogen bond formation because the oxygen atom is too little polarizable. This explains why the solubility of water in divinyl ether is as low as in benzene [1]. Diethyl ether, however, can form hydrogen bonds relatively easily as the CO π-bond order of this ether has about the same value as the $O' \ldots H$ σ-bond order in the hydrogen bond, see Tables IV and VI.

We are led to conclude that the energy of the hydrogen bond depends not only on electrostatic attraction but also on a certain delocalisation, *i. e.* polarisation, of the $2p$ electrons of the "hydrogen acceptor" atom. Quantitative conclusions about the degree to which these two effects contribute to the energy of the hydrogen bond cannot be drawn from the present investigation, because the values obtained for the delocalisation energies are too uncertain.

This work was started under the direction of Professor C. A. COULSON London. It is a pleasure for me to express my sincere thanks for his stimulating guidance during my stay in London and for his continued, helpful interest in my work. My thanks are also due to Fil. kand. Mrs. B. MOBACK, who assisted with the numerical calculations.

SUMMARY

Charge distribution and bond orders are calculated with the simple m. o. method for the following ethers: dimethyl, diethyl, divinyl, ethyl vinyl. The influence of the values chosen for the Coulomb integrals is discussed.

The m. o. method is also applied to the hydrogen bond of a molecular complex of ether-water. It is found that the $2p$ electrons of the etheral oxygen atom are delocalised to some extent through the hydrogen bond formation. Thus, the energy of the hydrogen bond is not purely electrostatic in origin.

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REFERENCES. 1. **L. Ehrenberg** and **I. Fischer**, Acta Chem. Scand. *2* (1948) 657. — **I. Fischer** and **L. Ehrenberg**, Acta Chem. Scand. *2* (1948) 669. — 2. **C. A. Coulson**, Quart. Rev. *1* (1947) 144. — 3. **G. W. Wheland**, J. Am. Chem. Soc. *63* (1941) 2025. — 4. **R. S. Mulliken, C. A. Rieke**, and **W. G. Brown**, J. Am. Chem. Soc. *63* (1941) 41. — 5. **L. Pauling**, J. Am. Chem. Soc. *54* (1932) 3570. — 6. **R. S. Mulliken**, J. Chem. Phys. *3* (1935) 573. — 7. **J. S. Roberts** and **H. A. Skinner**, Trans. Faraday Soc. *45* (1949) 339. — 8. **W. E. Duncanson** and **C. A. Coulson**, Proc. Roy. Soc. Edinb. A *62* (1943) 37. — 9. **C. A. Coulson** and **I. Fischer**, Phil. Mag. *40* (1949) 386. — 10. **C. A. Coulson**, Trans. Faraday Soc. *42* (1946) 106. — 11. **R. S. Mulliken**, Phys. Rev. *74* (1948) 736. — 12. **C. A. Coulson**, Trans. Faraday Soc. *33* (1937) 388. — 13. **L. L. Barricelli** and **O. Bastiansen**, Acta Chem. Scand. *3* (1949) 201.

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